

THE GASIFICATION OF WASTES USING MOLTEN SALTS

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INTRODUCTION

This paper describes some experimental results showing the technical feasibility of producing a low Btu gas (100-150 Btu/scf) from wastes using molten salt technology. The concept of molten salt gasification is described first and is followed by a description of the experimental apparatus. Then some results of bench scale gasification tests of selected wastes are given.

The disposal of waste x-ray film is discussed. While low Btu gas can be produced with film, a more important objective is to recover the silver from the film. Therefore, experiments to recover silver as well as experiments producing low Btu gas are described.

The discussion of film tests is followed by tests in which rubber tires and paper are gasified.

Then, some tests on the disposal of nitropropane are described. Organic NO_2 -containing compounds can be present in other wastes and, since they are a source of nitrogen oxides emissions due to their high nitrogen content, tests were carried out to determine if such wastes could be disposed of with low NO_x emissions.

The experimental portion of the paper concludes with a description of some gasification tests with sugar. Sugar was tested because it is a well-characterized oxygen containing substance and has a composition typical of many solid wastes.

A discussion of the results, including a comparison of these results with those of coal and oil gasification using the same technology, concludes the paper.

CONCEPT OF GASIFICATION OF WASTES WITH MOLTEN SALT

Molten Salt Gasification of wastes is a process which provides for the removal of pollutants during an initial partial oxidation and gasification step followed by complete burning of the clean combustible gases in a secondary combustor. Thus, the Molten Salt Gasification Process for the disposal of wastes is a two-step process.

In the first step, shredded combustible waste and air are continuously introduced beneath the surface of a sodium carbonate-containing melt at about $1,000^{\circ}\text{C}$. The waste is added in such a manner that any gas formed during combustion is forced to pass through the melt. Any acidic gases, such as HCl (produced from chlorinated organic compounds) and H_2S (from organic sulfur compounds) are neutralized and absorbed by the alkaline Na_2CO_3 . The ash introduced with the combustible waste is also retained in the melt. Any char from the fixed carbon is completely oxidized in the salt. The temperatures of gasification are too low to permit a significant amount of NO_x to be formed by fixation of the nitrogen in the air. Gasification of the waste is accomplished by using deficient air, i.e., less than the amount of air required to oxidize the waste completely to CO_2 and H_2O . Thus, in the first step, the waste is partially oxidized and completely gasified in the molten salt furnace. The gas generated has an effective heating value which depends upon the original waste. Values of approximately 150 Btu/scf have been obtained.

In the second step, this gas flows to a conventional gas-fired boiler in which it is combusted with secondary air, producing steam.

As a possible option, a sidestream of sodium carbonate melt can be withdrawn continuously from the molten salt furnace, quenched and processed

in an aqueous regeneration system which removes the ash and inorganic combustion products retained in the melt and returns the regenerated sodium carbonate to the molten salt furnace. The ash must be removed to preserve the fluidity of the melt at an ash concentration of about 20 weight %. The inorganic combustion products must be removed at some point to prevent complete conversion of the melt to the salts, with an eventual loss of the acid pollutant-removal capability.

This concept is the basis of the Molten Salt Coal Gasification Process which is currently being developed by Atomics International.

In the molten salt concept for silver recovery, the film is gasified in a Na_2CO_3 melt in the same manner as other combustible waste. The silver from the film forms a liquid metal pool which is drained from the bottom of the combustor to form metal ingots with a purity exceeding 99.9%.

EXPERIMENTAL

Materials

The waste x-ray film was analyzed and was found to contain in weight %: carbon, 53.2; hydrogen, 5.5; ash (which was essentially silver), 2.4; and the oxygen (by difference), 38.9. Direct analysis for silver showed that the film contained 2.3% silver. The wood was pine sawdust with a moisture content of 2.8%. No chemical analyses were carried out, but a typical composition for pine wood on a dry basis is: carbon, 51.8; hydrogen, 6.3; ash, 0.5; and oxygen, 41.3. The heating value is typically 9,130 Btu. The rubber was buffings from an automobile tire tread. No chemical analyses were carried out. The nitropropane was practical grade obtained from Eastman. The sugar consisted of pure sucrose. The Na_2CO_3 for the salt bath was technical grade material obtained from Kerr McGee.

Bench-Scale Molten Salt Gasifier

A cross-section view of the bench-scale molten salt gasifier is shown in Figure 1. Approximately 12 lb of molten salt are contained in a 6-in. ID

and 30-in. high alumina tube placed in a Type 321 stainless steel retainer vessel. This stainless steel vessel, in turn, is contained in an 8-in. ID, four-heating zone Marshall furnace. The four heating zones are each 8 in. in height, and the temperature of each zone is controlled by an SCR controller. Furnace and reactor temperatures are recorded by a 12-point Barber-Colman chart recorder.

Solids, pulverized when necessary in a No. 4 Wiley mill to <1 mm in particle size, are metered into the 1/2-in. OD central tube of the injector by a screw feeder. Rotation of the screw feeder is provided by a 0 to 400 rpm Eberback Corporation Con-Torque stirrer motor. In the injector the solids are mixed with the air being used for gasification, and this solids-air mixture passes downward through the center tube of the injector and emerges into the 1-1/2-in. ID alumina feed tube. This alumina feed tube is adjusted so that its tip is $\sim 1/2$ in. above the bottom of the 6-in. diameter alumina reactor tube. Thus, the solids-air mixture is forced to pass downward through the feed tube, outward at its bottom end, and then upward through ~ 6 in. of salt in the annulus between the 1-1/2-in. and the 6-in. alumina tubes. In the case of liquids, a different feed system is used. The liquid is pumped with a laboratory pump and is sprayed into the alumina feed tube.

In order to prevent the melt temperature from rising when an excessive amount of heat is released to the melt, a cooling system (not shown in Figure 1) cooled by air, maintained a constant temperature. It consists of an eight-hole air distribution ring, mounted underneath the stainless steel ceramic tube retainer vessel. Air at rates up to 18 cfm can be passed upward between the outer surface of the retainer vessel and the furnace wall.

Off Gas Analyses

Samples of the exit gas, for analysis by gas chromatography, are taken with 1-ml gastight syringes downstream of the CO_2 analyzer. Two gas samples

are taken at the same time. One sample is analyzed for carbon monoxide, oxygen, and nitrogen, using a molecular sieve 13X column at room temperature. The other sample is analyzed for carbon dioxide, methane, ethane, ethylene, sulfur dioxide, and hydrogen sulfide, using a Poropak Q column at 130°C (266°F). Often, continuous measurements of NO_x, CO, and CO₂, are taken of the off-gas. The NO_x analyses are made with a Thermo Electron Corporation Chemiluminescent NO_x Analyzer. The carbon monoxide and carbon dioxide determinations are made with Olson-Horiba, Inc. units. (Mexa-300 carbon monoxide and Mexa-200 carbon dioxide analyzers, respectively.) All gas analysis data are reported on a dry basis.

Results

The gasification steady state results for film, wood, rubber, and nitropropane are shown in Table 1. The results for sucrose are shown in Table 2.

Film

Two series of tests were carried out with waste x-ray film. The purpose of the first test (No. 1) was to show that pure elemental silver could indeed be recovered under gasification conditions attainable in the Atomics International pilot plant which is capable of gasifying about 200 lbs/hr of coal and waste. A combustible gas with a higher heating value (HHV) of 100 Btu/scf was obtained. In this bench scale test, 15 lbs of film were burned. After the test, the melt was cooled until the silver solidified (960°C). A bright pellet of lustrous silver metal having a weight of 0.34 lbs was recovered. This corresponds to 98.6% of the silver in the film feed. Because of the successful results of this bench scale tests, a test to recover film from 20,000 lbs of waste x-ray film is planned for the near future. (A silver recovery test in the Atomics International's pilot plant has been carried out in which 15,000 lbs of waste x-ray film were burned under excess air conditions at a rate of 100 lbs/hr. In that test, which was carried out for the Navy, a single silver metal ingot weighing 230 lbs with 99.9% purity was recovered.)

In test No. 2, the gasification was carried out under more reducing conditions (22% theoretical air). This time a gas with a much higher heat content was obtained (179 Btu/scf). Elemental silver was recovered from this test also but the yield was not determined.

Wood

Gasification of the pine wood was carried out with 30% theoretical air. Again, a gas with a high heat content (181 Btu/scf) was obtained. The H_2 content was somewhat higher and the CH_4 content somewhat lower than was obtained with the film at 22% theoretical air. However, it is not clear whether this difference is real.

Rubber

Two tests were carried out with rubber from a rubber tire. Since the tire contained organic sulfur which would form Na_2S in the melt, the Na_2CO_3 melt originally contained 6 wt % Na_2S to simulate steady state conditions. Sodium sulfide was also added because it has been established at Atomic International and other laboratories that Na_2S is a catalyst in accelerating the gasification of char in molten Na_2CO_3 . The gasification was carried out with 33% theoretical air. The results in Table 1 are an average of the two tests. A gas with an HHV of 156 Btu/scf was obtained. The CO_2 content of this gas was considerably lower than that from the oxygen-containing wastes and is more similar to that obtained when coal or oil is gasified. In spite of the large amounts of Na_2S in the melt, no H_2S or other sulfur-containing gases (<30 ppm) were detected in the off gas.

Nitropropane

Organic NO_2 -containing compounds may well be present in small amounts in wastes which are being gasified for producing fuel. This type of compound

can emit a great deal of NO_x . In these tests, nitropropane was used to determine if it would be possible to minimize the NO_x emissions during gasification. A series of tests was run under varying conditions and with different additives. It was determined that under certain process conditions and with a specific additive, it was possible to combust nitropropane and produce a product gas containing only 6 ppm NO_x . It thus appears that the presence of organic NO_2 -containing wastes will not contribute much NO_x under gasifying conditions. The composition of a typical off gas from the tests is shown in Table 1.

Sucrose

The gasification of sucrose in pure Na_2CO_3 was studied at four different stoichiometries. The melt temperature was about 950°C . The air feed rate (2.5 scfm) corresponded to an air superficial velocity in the gasifier of 1 ft/sec. As expected, the heating value of the gas increased as the percent theoretical air decreased. However, when the air/fuel ratio was too low, insufficient heat was released to the melt and auxiliary heating was required. This was the case with the test in which 18% theoretical air was used. The furnace was turned on during the test to maintain the melt temperature. However, at 35 and 52% theoretical air, sufficient heat was released to the melt so that the furnace could be turned off. At 72% air, excess heat was generated and had to be removed by the cooler. The relatively short experimental runs (~1 hour) did not permit a definite conclusion as to what minimum percent of theoretical air could be used in this system and still maintain melt temperature without auxiliary (furnace) heat. It appears, however, that the salt could be maintained in a molten state at least at 35% of theoretical air at which level a combustible gas with an HHV of 154 Btu/scf was being generated.

A test in which the air superficial velocity was reduced to 1/2 ft/sec yielded an off-gas virtually unchanged in composition to that when the velocity was 1 ft/sec. This suggests that residence time in the melt is not an important factor.

Discussion

It is of interest to compare the heating value of a gas produced from a material containing a great deal of combined oxygen with that produced from a conventional fuel such as coal and fuel oil. A comparison of the heating values of gases produced by the oxygenated compounds which contain 40-50 wt % oxygen, by Kentucky No. 9 coal (7 wt % oxygen), and by No. 6 fuel oil (essentially no oxygen) using the same molten salt technology is shown in Table 3. It can be seen that the difference in heating value of the gas is relatively small in spite of the large difference in Btu content of the combustible material (12,000 Btu/lb for the coal and 19,000 Btu/lb for the fuel oil vs 7,000-9,000 Btu/lb for the oxygenated material). The small difference in heat content of the gases probably is due in part to the fact that a great deal of the oxygen is supplied by the fuel and this combined oxygen is not diluted with atmospheric nitrogen. To illustrate, the nitrogen contents of the off gas were 59% in the case of fuel oil at 20% theoretical air and only 34% in the case of sucrose at 18% theoretical air.

It has been shown that, as expected, the Btu content of the off-gas increases as the percent of theoretical air decreases. However, as was also shown (in test No. 6), there is a practical upper limit on the gas heat content which can be obtained. Above this upper limit, there will not be enough heat released to the melt to sustain the operating temperature. This upper limit can be increased somewhat by using preheated process air and by decreasing the heat losses in the gasifier with improved insulation.

The maximum waste throughput is also governed by the maximum superficial velocity of the gas through the melt. In general, the maximum superficial velocity of the inlet air has been set at 2 ft/sec. (This corresponds to a somewhat higher velocity of the product gas, depending on the fraction of total oxygen which is combined oxygen and on the composition of the off-gas.) Beyond this velocity of 2 ft/sec, entrainment of the melt becomes excessive. However, by operating at elevated pressures, the waste throughput can be significantly increased since at a given air superficial velocity, the waste throughput will be proportional to the pressure.

No sulfur-containing pollutants were observed in the off-gas when rubber was gasified. While chlorine-containing material was not gasified, in all tests in which that type of material was treated in Na_2CO_3 melts with excess air, there was no trace of HCl even when the Na_2CO_3 content was as low as 5 wt %. It is expected that the same results would be obtained if deficient air were used.

The results described in this paper show that the gasification of wastes in molten salts to produce a low Btu gas is technically feasible. However, an engineering evaluation leading to the economics of molten salt gasification of the various wastes has not been done and would be necessary before it can be established if this process is a practical one.

TABLE 1

Gasification of Wastes

Test #	Waste	Temp. (°C)	Air Feed Rate (scfm)	Fuel Feed Rate (lb/hr)	% Theor (a) Air	Composition of Off-Gas (vol %)					Higher Heating (b) Value (Btu/scf)
						CO ₂	CO	H ₂	CH ₄	C ₂	
1	Film	1015	4.50	5.34	51	16.5	12.0	11.7	2.6	0.2	107
2	Film	958	2.50	6.58	22	16.0	18.3	14.1	5.2	1.2	179
3	Wood	951	1.00	2.08	30	14.5	20.3	21.1	3.0	0.9	181
4	Rubber	920	1.63	1.81	33	4.0	18.4	16.0	2.4	1.1	156
5	Nitropropane	1000	2.50	2.58	75	11	8	9	NM ^(c)	NM ^(c)	>55

(a) Percent of air required to oxidize material completely to CO₂ and H₂O

(b) Calculated from composition of off-gas

(c) Not measured

TABLE 2
Gasification of Sucrose in 100% Na_2CO_3 (a)

Test #	Solid Feed Rate (lb/hr)	% Theor. Air (b)	Composition of Off-Gas (vol %)					Higher Heating (c) Value Btu/scf
			N_2	CO_2	CO	H_2	CH_4	
6	12.2	18.4	34.3	13.5	26.9	18.9	4.3	216
7	6.5	34.8	46.2	15.0	18.3	17.0	2.5	154
8	4.3	52.2	57.0	19.1	12.3	9.7	1.4	91
9	3.1	72.1	69.8	20.0	5.5	3.1	0.7	37
							C_2	
							1.9	
							0.8	
							0.3	
							0.1	

- (a) The melt temperature was 950-960°C. The air feed rate was 2.5 scfm
 (b) Percent of air required to oxidize material completely to CO_2 and H_2O
 (c) Calculated from composition of off-gas

TABLE 3

A Comparison of the Heating Value of Gas
Produced from Sucrose and from Coal

OXYGENATED MATERIAL			CONVENTIONAL FUELS		
Material	% Theor. Air	HHV Btu/scf	Fuel	% Theor. Air	HHV Btu/scf
Sucrose	18	216	Fuel Oil ^a	20	191
Film	22	179	Fuel Oil	27	155
Wood	30	181	Coal ^b	35	151
Sucrose	35	154	Coal	40	138
Film	51	107	Coal	50	118
Sucrose	53	91	Coal	70	36
Sucrose	72	37			

(a) The fuel oil was a No. 6 oil. It was API gravity 18, carbon residue, 5%; ash, 0.007%; sulfur, 0.3%, hydrogen 13%.

(b) The coal was Kentucky No. 9 seam coal. The proximate analysis on a dry basis was in weight %; ash, 16.4; volatile matter, 37.6; fixed carbon, 46.0; and sulfur, 4.5. The ultimate analysis on a dry basis was: carbon, 66.3; hydrogen, 4.6; nitrogen, 1.4; sulfur, 4.5; ash, 16.4; and oxygen (by difference), 6.9.

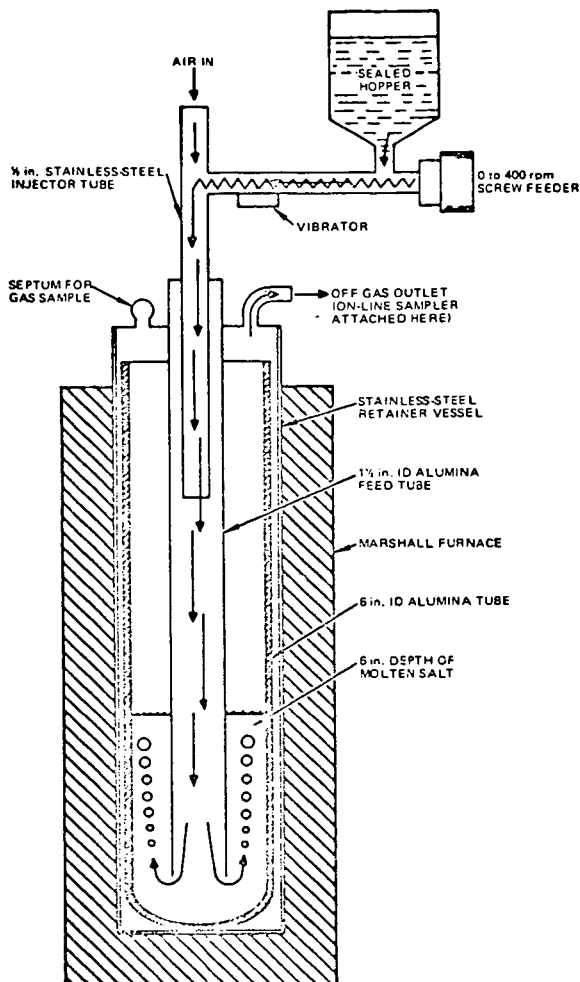


Figure 1. Bench Scale Molten Salt Gasifier Schematic